Catalytic synthesis of alcoholic fuels for transportation from syngas - DTU Orbit

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This work has investigated the catalytic conversion of syngas into methanol and higher alcohols. Based on input from computational catalyst screening, an experimental investigation of promising catalyst candidates for methanol synthesis from syngas has been carried out. Cu-Ni alloys of different composition have been identified as potential candidates for methanol synthesis. These Cu-Ni alloy catalysts have been synthesized and tested in a fixed-bed continuous-flow reactor for methanol synthesis. The metal area based activity for a Cu-Ni/SiO2 catalyst is at the same level as a Cu/ZnO/Al2O3 model catalyst. The high activity and selectivity of silica supported Cu-Ni alloy catalysts agrees with the fact that the DFT calculations identified Cu-Ni alloys as highly active and selective catalysts for the hydrogenation of CO to form methanol. This work has also provided a systematic study of Cu-Ni catalysts for methanol synthesis from syngas. The following observations have been made: (1) Cu-Ni catalysts (Cu/Ni molar ratio equal to 1) supported on SiO2, ZrO2, γ-Al2O3, and carbon nanotubes exhibit very different selectivities during CO hydrogenation. However, the metal area based CO conversion rates of all supported Cu-Ni catalysts are at the same level. Carbon nanotubes and SiO2 supported Cu-Ni catalysts show high activity and selectivity for methanol synthesis. The γ-Al2O3 supported Cu-Ni catalyst has a significant amount of acid sites and produces predominantly dimethyl ether. The Cu-Ni/ZrO2 catalyst exhibits high methanol selectivity at lower temperatures (250 °C), but the selectivity shifts to hydrocarbons and dimethyl ether at higher temperatures (> 275 °C). It seems likely that the Cu-Ni alloys always produce methanol, but that some supports further convert methanol to different products. A combination of in situ XAS, XRD and TEM studies on supported Cu-Ni catalysts shows that the support influences the reduction processes and consequently the formation of Cu-Ni alloys and their CO hydrogenation properties. (2) Cu-Ni/SiO2 catalysts have been prepared with different calcination and reduction procedures and tested in the synthesis of methanol from H2/CO. The calcination of the impregnated catalysts (with without calcination step) and different reduction procedures with varying hydrogen concentration have significant influence on Cu-Ni alloy formation and the alloy particle size and consequently on the catalytic activity. (3) Addition of 3 mol % CO2 to the H2/CO feed stream leads to a significant loss of activity for the Cu-Ni/SiO2 catalyst contrary to the case for the Cu/ZnO/Al2O3 catalyst. DFT calculations show in accordance with previous surface science studies that oxygen on the surface (one of the intermediates from water gas shift reaction) could lead to an enrichment of the Ni-content in the surface. Co-fed CO2 in the syngas should result in an increased oxidative potential of the feed, and this could cause a change of the surface composition and hence the catalytic performance. (4) Silica supported bimetallic Cu-Ni catalysts with different ratios of Cu to Ni have been prepared by impregnation. In situ reduction of Cu-Ni alloys with combined synchrotron XRD and XAS reveal a strong interaction between Cu and Ni, resulting in improved reducibility of Ni as compared to monometallic Ni. At high nickel concentrations silica supported Cu-Ni alloys form a homogeneous solid solution of Cu and Ni, whereas at lower nickel contents, copper and nickel are separately aggregated and form metallic Cu and Cu-Ni alloy phases. At the same reduction conditions, the particle sizes of reduced Cu-Ni alloys decrease with increasing in Ni content. The activity tests of Cu-Ni alloys show that all Cu-Ni alloys produce mainly methanol during CO hydrogenation regardless of the Cu/Ni ratio. The Cu-Ni alloy catalysts show similarities in the selectivity, which is mainly towards methanol (~99 mol %), while exhibiting differences in methanol productivity. The methanol productivity reaches a maximum in the molar ratio of around 1. One possibility is that the active surface structure is similar for all Cu-Ni alloys, but the number of active sites varies with respect to the ratio of Cu to Ni. (5) The effect of catalyst preparation methods has been evaluated. Silica supported Cu-Ni catalysts have been prepared via impregnation, co-precipitation, and deposition-co-precipitation and tested for methanol synthesis. It is found that co-precipitation and deposition-co-precipitation methods are more efficient than the impregnation method for preparation of small and homogeneous Cu-Ni alloy nanoparticles. The selectivity towards methanol is always higher than 99 mol %, and the metal area based methanol formation rate over these catalysts is at the same level regardless of the preparation method. The methanol productivity increases in the order of impregnation < co-precipitation < deposition-co-precipitation. The increase in activity is predominantly caused by a decrease in particle size of the active metal alloy particles. A maximum methanol productivity of 0.66 kg kgcat-1 h-1 with methanol selectivity up to 99.2 mol % has been achieved for a Cu-Ni/SiO2 catalyst prepared by the deposition-co-precipitation method. (6) There is no apparent catalyst deactivation observed during the tested time on stream (40-100 h), contrary to the observation for the industrial Cu/ZnO/Al2O3 catalyst.

For higher alcohol synthesis, the main work has been performed on CO hydrogenation over supported Mo2C. Mo2C supported on active carbon, carbon nanotubes, and titanium dioxide, and promoted by K2CO3, has been prepared and tested for higher alcohol synthesis from syngas. At optimal conditions, the activity and selectivity to alcohols (methanol and higher alcohols) over supported Mo2C are significantly higher compared to bulk Mo2C. The CO conversion reaches a maximum, when about 20 wt % Mo2C is loaded on active carbon. The selectivity to higher alcohols increases with increasing Mo2C loading on active carbon and reaches a maximum over bulk Mo2C, while the selectivity to methanol follows the opposite trend. The effect of Mo2C loading on the alcohol selectivity at a fixed K/Mo molar ratio of 0.14 could be related to the amount of K2CO3 actually on the active Mo2C phase and the size, structure, and composition of the supported carbide clusters. Unpromoted, active carbon supported Mo2C exhibits a high activity in CO hydrogenation with hydrocarbons as the dominant products. The K2CO3 promoter plays an essential role in directing the selectivity to alcohols rather than to hydrocarbons. The optimum selectivity towards higher alcohols and alcohols in general is obtained at a K/Mo molar ratio of 0.21 over the active carbon supported Mo2C (20 wt %). Combined in situ XAS and XRD have been used to follow directly the carburization process and formation of bulk and supported molybdenum carbides (20 wt % and 40 wt % Mo2C on active carbon). The bulk Mo2C prepared by temperature programmed carburization in flow of 20 mol % CH4 in H2 most likely adopts an orthorhombic structure (α-Mo2C). A two-step mechanism is discovered during the in situ carburization process, composed of the initial reduction of Mo(VI) oxide to Mo(IV) oxide followed by a succeeding conversion to carbide. The necessary carburization temperature is to a significant extent determined by the crystal sizes. A decrease on particle size can initiate the onset of carburization at a lower
temperature.

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